⊗ Dissociation 8.3 2012-3

* Process in which ionic molecules seperates into smaller molecules (ions), usually in a reversible manner

example $NaCl \rightleftarrows Na^+ + Cl^-$

Ion product of water

$$H_2O \rightleftarrows H^+ + OH^-$$

$$K_{eq} = \frac{[H^+]\cdot[OH^-]}{[H_2O]} = \frac{10^{-7}\,10^{-7}}{55}$$

Concentration of water 'always' 55 M in dilute solutions

$$K_w \equiv K_{eq}\,[H_2O] = [H^+]\,[OH^-] = (10^{-7})^2$$

ion product of water at room temperature (always hold

Define $pH \equiv -\log_{10}[H^+]$ $pOH \equiv -\log_{10}[OH^-]$

$$pH + pOH = -\log_{10}\left([H^+][OH^-]\right) = -\log_{10}(10^{-14}) = 14$$

Water $pH = 7$ neutral

$[H^+]$ increases $\Rightarrow$ pH decreases $pH < 7$ acidic

$[H^+]$ decreases $\Rightarrow$ pH increases $pH > 7$ basic

examples

Hydrogen cloride $HCl \rightleftarrows H^+ + Cl^-$ increases $[H^+]$ acid

Sodium hydroxide $NaOH \rightleftarrows Na^+ + OH^-$ increases $[OH^-]$ decreases $[H^+]$ base

Add both ($\Rightarrow pH = pOH = 7$)

$H^+ + OH^-$ combined into water

$Na^+ + Cl^-$ combined into NaCl (salt)

Fraction of protonated molecules

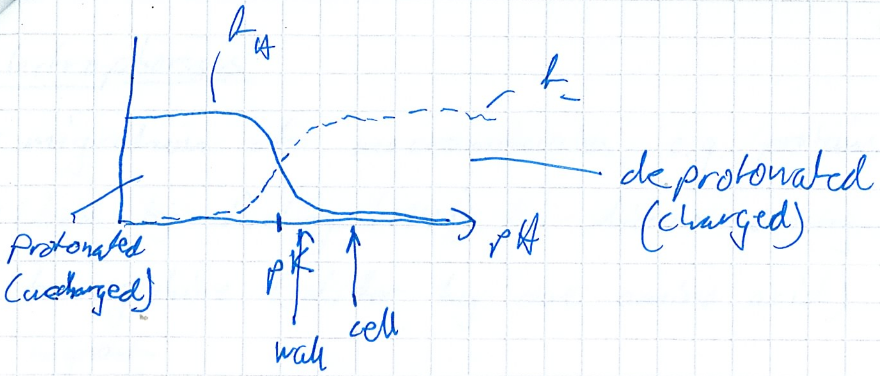
example auxin (weak acid), $AH \rightleftarrows A^- + H^+$

$$K_{eq} = \frac{[A^-][H^+]}{[AH]} \qquad \left([A^-] = K_{eq}\frac{[AH]}{[H^+]}\right)$$

$$f_H = \frac{[AH]}{[AH]+[A^-]} = \frac{[AH]}{[AH]\left(1+K_{eq}/[H^+]\right)} = \frac{1}{1+10^{pH-pK}}$$

{ fraction/probability of protonation }

$$f_c = \frac{[A^-]}{[AH]+[A^-]} = \frac{1}{1+10^{-(pH-pK)}} = 1 - f_H$$



In plants

Only AH (protonated form) can diffuse through membrane

$$A_{cell} \rightleftarrows A_{wall}$$

$f_H \sim 0.002$ $f_H \sim 0.3$

∴ Auxin needs help to get out of cells

example base

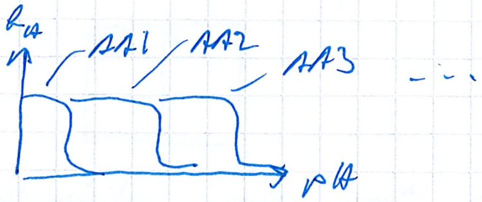
$M-NH_3^+ \rightleftarrows M-NH_2 + H^+$ ∴ charged when protonated

Proteins

- sequence of amino acids (AA) with different pK [3, 7, 12.5]
- sequence ⇒ 3D structure ⇒ function

acidic side chain $-COOH \rightleftarrows -COO^- + H^+$

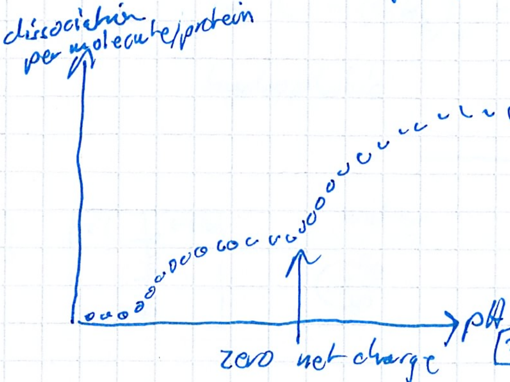
basic side chain $-NH_3^+ \rightleftarrows -NH_2 + H^+$



low pH most Amino acids protonated < bases positive charge / acids neutral

high pH most amino acids deprotonated < bases neutral / acids negative charge

Titrations (low → high pH)

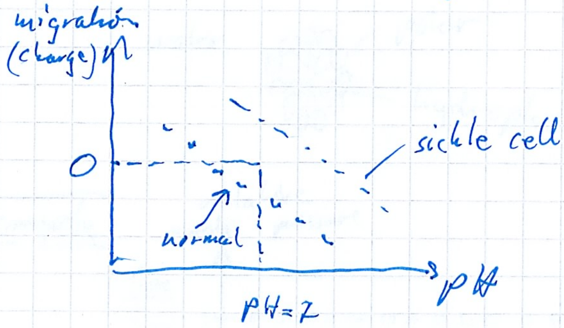


∴ Finger print for proteins

Can resolve protein composition

Electrophoresis

- migration of macromolecules, e.g. proteins, in an electric field
- Used by Pauling (1949) to dicern among normal and "sickle-cell" hemoglobine (differ by one amino acid)

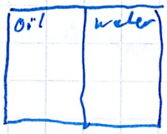


opposite charge at pH = 7

⊛ Self assembly of amphiphiles 8.4

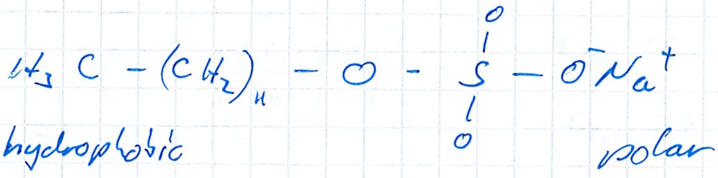
- Fundamental structures in the cell (e.g. membranes) can self-assemble by following chemical forces, in particular hydrophobic interaction
  - hydrophilic (polar) molecules mix freely with water (make hydrogen bonds)
  - hydrophobic (non-polar) molecules does not mix freely with water (disrupt hydrogen bonds)

example



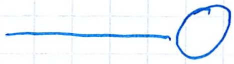
  - amphiphiles one part of the molecule is polar the other hydrophobic (emulsifier, surfactants, detergents, phospholipid

example sodium dodecyl sulfate (SDS)

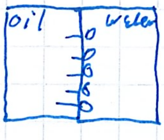


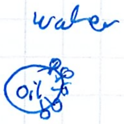
$$H_3C-(CH_2)_{11}-O-\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{S}}-O^-Na^+$$

hydrophobic polar



examples



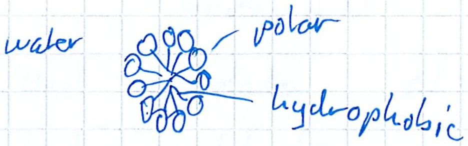


Mayonnaise

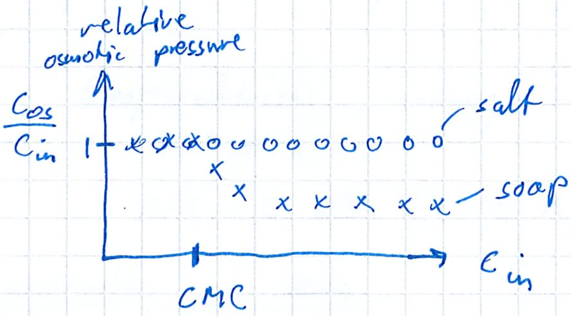
oil+"water" + egg (phospholipid (lecithin)

Micelles

- spheres of surfactants molecules
- self-assemble suddenly at critical concentration
- hydrophobic effect



example



$P_{os} \propto c_{os} = \frac{N_{obj}}{V}$ (ch. 7)

c_{in} = added concentration (undissociated)

CMC critical micelle concentration

above this concentration, the ratio of independently moving objects to all ions drops steeply

Model

$(YX \rightleftarrows X_1 + Y)$

$N X_1 \rightleftarrows X_N \qquad \frac{c_N}{(c_1)^N} = K_{eq}$

$c_{tot} = c_1 + N c_N = c_1 + N K_{eq} c_1^N = c_1 \left(1 + N K_{eq} c_1^{N-1}\right)$ (a)

CMC, c_*, value of c_{tot} where $\begin{cases} c_{1*} = \frac{1}{2} c_* \\ N c_{N*} = \frac{1}{2} c_* \end{cases}$

$$\left(\frac{1}{2N} c_*\right)\left(\frac{1}{2} c_*\right)^{-N} = K_{eq} \Rightarrow N K_{eq} = \left(\frac{2}{c_*}\right)^{N-1} \text{(b)}$$

$$\boxed{\underset{\uparrow \atop a,b}{c_{tot}} = c_1 \left(1 + \left(\frac{2c_1}{c_*}\right)^{N-1}\right)}$$

$c_{tot} \ll c_* \Rightarrow c_{tot} \sim c_1$

$c_{tot} \gg c_* \Rightarrow c_{tot} \sim c_1^N \underbrace{\left(\frac{2}{c_*}\right)^{N-1}}_{N K_{eq}} \sim N c$

relative osmotic pressure $= \dfrac{(c_{tot} + c_1 + c_N)\, k_B T}{2\, c_{tot}\, k_B T} =$

micelles as one

$$= \frac{1}{2}\left(1 + \frac{c_1(1+K_{eq}\,c_1^{N-1})}{c_1(1+NK_{eq}\,c_1^{N-1})}\right) = \frac{1}{2}\left[1 + \frac{c_1\left(1+\frac{1}{N}\left(\frac{2c_1}{c_*}\right)^{N-1}\right)}{c_1\left(1+\left(\frac{2c_1}{c_*}\right)^{N-1}\right)}\right]$$

micelles as N

$NK = \left(\frac{2}{c_*}\right)^{N-1}$

Fitted to data $N=30$ $c_* = 1.4\,\text{mM}$ (Fig 8.6)

∴ Simple model (2 parameters) explain qualitative features

exercise? Cooperativity, many monomers cooperate to create mice

$$YX \rightleftarrows X_1 + Y$$

$$NX_1 + E \rightleftarrows C \rightarrow X_N + E \qquad \frac{dx_N}{dt} = f(x_1) \;?$$

Self-assembly in cells

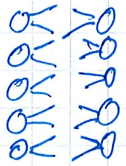
Two-tailed amphiphiles  e.g. phospo lipids (Fig 8.3)

- hard to form micelles due to space constrictions

$N\, a_{head} \sim 4\pi R^2$ relation between a_{head}

$N\, v_{tail} \sim \frac{4\pi R^3}{3}$ and v_{tail} must be fulfilled

- prefer bilayer structures

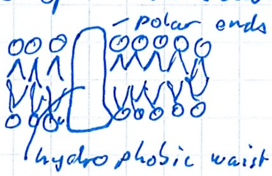


- two hydrophobic chains ⇒ double cost for tails exposed to water $\{$cf. $e^{-\epsilon/k_BT}$ vs $e^{-2\epsilon/k_BT}\}$ ⇒ CMC small
- closed "bags" leads to no boundary to water

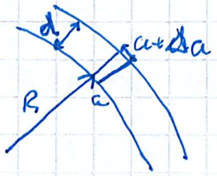
large "cells" ok

(organic?) - easy for cells to synthesize phospholipids also from non-living systems

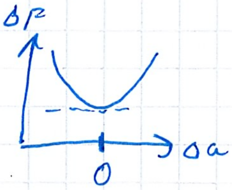
- membranes are thin, tough and scarcly permeable to ions
- fluid character ⇒ shape changes possible
- accept embedded objects (doorways to cells)



Bending stiffness of membranes



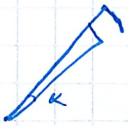
Cylinder (1D bending)



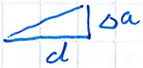
$\Delta a = 0 \iff$ minimal free energy

$$\Delta F = \underset{\substack{\downarrow \\ \text{const } c}}{\Delta F\Big|_{\Delta a=0}} + \underset{\substack{\downarrow \\ =0\ (\text{minimum})}}{\frac{\partial \Delta F}{\partial \Delta a}\Big|_{\Delta a=0}} \Delta a + \frac{1}{2} \underset{\substack{\downarrow \\ \frac{1}{2}k}}{\frac{\partial^2 \Delta F}{\partial \Delta a^2}} \Delta a^2 + O(\Delta a^3)$$

elastic energy per phospholipid molecule $\frac{1}{2} k \Delta a^2$



$\alpha = \frac{a}{R}$



$\sin\alpha \approx \alpha = \frac{\Delta a}{d}$

$$\frac{a}{R} = \frac{\Delta a}{d}$$

$$\Delta a = \frac{ad}{R}$$

$$\Delta F = \frac{1}{2} k \left(\frac{ad}{R}\right)^2$$

$$\begin{Bmatrix} \frac{1}{2} N a = A \\ N/A = \frac{2}{a} \end{Bmatrix}$$

bend stiffness, $K \equiv 2kd^2$

$\therefore$ ΔF per unit area to bend a bilayer membrane into cylinder R is of the form $\frac{1}{2} K/R^2$

Sphere $\Rightarrow$ Δa in two directions

ΔF per unit area $2K/R^2$, $A = 4\pi R^2$

Bend onto sphere $8\pi K$ $\Rightarrow$ independent of radius!